

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-00-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for review the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

0795

| | | | | | |
|--|--|---|--|---|--|
| 1. AGENCY USE ONLY (Leave blank) | | 2. REPORT DATE August 31, 2000 | | 3. REPORT TYPE AND DATES COVERED Final Technical Report: 3/1/96 to 8/31/99 | |
| 4. TITLE AND SUBTITLE Corrosion Protection of Aluminum and its Alloys Using Electroactive Polymers | | | | 5. FUNDING NUMBERS F49620-96-1-0080 | |
| 6. AUTHOR(S) Arthur J. Epstein | | | | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Arthur J. Epstein Distinguished University Professor Department of Physics The Ohio State University 174 W. 18 th Ave. Columbus, OH 43210 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER | |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Charles Y.-C. Lee Program Manager AFOSR-NL 801 N. Randolph Street Room 732 Arlington, VA 22203-1977 | | | | 10. SPONSORING / MONITORING AGENCY REPORT NUMBER | |
| 11. SUPPLEMENTARY NOTES | | | | | |
| 12a. DISTRIBUTION / AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED | | | | 12b. DISTRIBUTION CODE | |
| 13. ABSTRACT (Maximum 200 Words) The AFOSR funded program was designed to specifically test the ability of electroactive polymers, especially polyanilines, to provides corrosion protection for aluminums, especially the copper (~ 4 to 5%) containing AA2024-T3 alloy of key interest to the Air Force. This program demonstrated the anti-corrosion capability of polyaniline coatings on aluminum alloy 2024-T3. In particular, undoped emeraldine base, fully sulfonated polyaniline (NSPAN), and undoped trimer coatings on AA2024-T3 were shown to reduce pitting in argon deaerated 0.1M NaCl using potentiodynamic polarization studies. The corrosion potential was shifted to more noble, and corrosion current was reduced 100- to 1000-fold in pH ≥ 3 environments. The anti-corrosion capability of emeraldine base polyaniline coatings of AA2024-T3 in 0.1M NaCl further was been demonstrated by X-ray photoelectron spectroscopy (XPS) depth profiling which showed a clear depletion of Cu for ≥ 500 Å. Visual inspections demonstrated the effectiveness of sulfonated polyaniline solutions at preventing corrosion of aluminum and iron alloys. A new mechanism of corrosion reduction in aluminum alloys (different from that operative in ferrous alloys) was proposed, i.e., copper depletion by an active polymer such as polyaniline at the corroding surface | | | | | |
| 14. SUBJECT TERMS Corrosion, Aluminum, Polymers | | | | 15. NUMBER OF PAGES 18 | |
| | | | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OF REPORT Unclass | 18. SECURITY CLASSIFICATION OF THIS PAGE Unclass | 19. SECURITY CLASSIFICATION OF ABSTRACT Unclass | | 20. LIMITATION OF ABSTRACT | |

20010109 043

Final Technical Report
August 31, 2000

Grant Title: *Corrosion Protection of Aluminum and its Alloys Using Electroactive Polymers*

Grant Number: F49620-96-1-0080

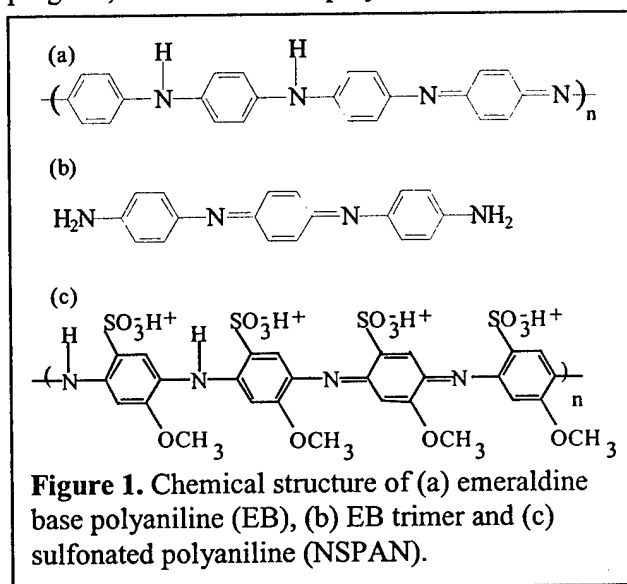
Grant Principal Investigator: Arthur J. Epstein
Department of Physics & Department of Chemistry
The Ohio State University
Columbus, Ohio 43210-1106

Telephone: 614-292-3706
Fax: 614-292-3706
E-mail: Epstein.2@osu.edu

Grant Period: March 1, 1996 – August 31, 1999

1. Summary of the most significant accomplishments in this program.

The objective of this program was to determine the potential of electroactive polymers in inhibiting the corrosion of aluminum and its alloys. At the start of the three year AFOSR funded program, several forms of polyaniline had been shown to provide corrosion protection capability



for iron and its alloys, but the reports of the effectiveness of electroactive polymers in corrosion protection of aluminum had been scattered and conflicting. This AFOSR sponsored program was successful in discovering and demonstrating the effectiveness of several polyaniline-based electroactive polymer coatings in substantially reducing corrosion of copper containing aluminum alloys. The mechanism of protection was discovered to be preferential copper extraction from the alloy surface, distinctly different then the corrosion protection mechanism provided by iron-based alloys by polyanilines. Further, this AFOSR program discovered a new corrosion protection phenomenon - the

effectiveness of aqueous solutions of sulfonated polyaniline in preventing corrosion of copper containing aluminum and also cold rolled steel coupons immersed in these solutions.

The AFOSR funded program was designed to specifically test the ability of electroactive polymers, especially polyanilines, to provides corrosion protection for aluminums, especially the copper (~ 4 to 5%) containing 2024-T3 alloy of key interest to the Air Force. Our program demonstrated the anti-corrosion capability of polyaniline coatings on aluminum alloy 2024-T3. In particular, undoped emeraldine base, sulfonated polyaniline, and undoped trimer (Figure 1) coatings on aluminum alloy AA2024-T3 were been shown to reduce pitting in argon deaerated 0.1M NaCl using potentiodynamic polarization studies. The anti-corrosion capability of emeraldine base polyaniline coatings of aluminum alloy 2024-T3 in 0.1M NaCl further was been demonstrated by X-ray photoelectron spectroscopy (XPS) depth profiling. Visual inspections demonstrated the effectiveness of sulfonated polyaniline solutions at preventing corrosion of aluminum and iron alloys. A new mechanism of corrosion reduction in aluminum alloys was proposed, i.e., copper depletion by an active polymer such as polyaniline at the corroding surface.

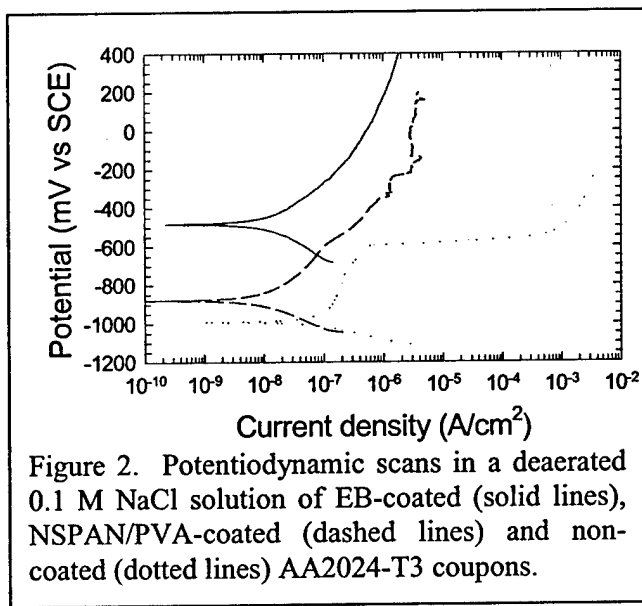
For potentiodynamic polarization studies, polymer coated and uncoated aluminum AA2024-T3 coupons (AA2024-T3, from McMaster Carr Supply Inc., 4.4%Cu, 0.6%Mn, 1.5% Mg, 1.5 x 1.5 x 0.07 cm³ coupons) were placed in the holder of the bottom of a vessel with the coated side exposed to the 0.1M NaCl solution. Electrochemical polarization measurements were carried out using a Potentiostat model 273A (EG & G / PARC) controlled by the M352/252 corrosion software applying a sweep rate of 0.5 mV/s. A standard three-electrode

configuration with a saturated calomel reference electrode and a platinum counter electrode was used. The exposed area of the working electrode (alloy coupon placed at the bottom of the cell with coated side facing to electrolyte) was 0.8 cm^2 .

Polarization scans were performed in the noble direction after allowing the steady state potential to develop. The experiments were carried out at room temperature in aerated 0.1 M NaCl solution with various pH. The pH of the solution was adjusted using H_2SO_4 or NaOH . In all cases triplicate experiments were carried out to ensure reproducibility. A new alloy coupon was used for each run Polished (600 grit) AA2024-T3 coupons were prepared and $\sim 20 \text{ }\mu\text{m}$ EB films were drop cast from a 12 mg/ml NMP solution. Coupons coated with sulfonated polyaniline (NSPAN), Figure 1c, also were prepared by first spin coating a $\sim 2000 \text{ }\text{\AA}$ thick film of water-dissolved poly(vinyl alcohol) (PVA) onto the metal surface. This film was then heated to $150 \text{ }^\circ\text{C}$ for 10 min in order to facilitate cross linking and improve adhesion. After cross linking, a 1:4 blend of PVA and NSPAN was spun from an aqueous solution on top of the PVA film, where upon the samples were heated again to $150 \text{ }^\circ\text{C}$ for 10 minutes in order to crosslink the NSPAN/PVA blend. The coupons were exposed to electrolyte for 10 minutes prior to potentiodynamic data acquisition. Typically, the corrosion current measured for the coated coupons was tenfold reduced from that of the uncoated AA2024-T3 coupons, indicating much lower corrosion rates. Pitting corrosion was observed on the uncoated sample, but no pitting was recorded for the coated samples.

For XPS studies the coated and non-coated samples were immersed in 0.1 M NaCl solutions kept at RT for 10 to 66 h. Prior to insertion into the ultra high vacuum chamber, the

coatings were removed by lifting up on a corner. XPS depth profiling was then carried out. Pristine (though same polishing treatment) AA2024-T3 coupons were studied as well. A VG Scientific ESCALAB MkII XPS spectrometer with $\text{Mg K}\alpha$ X-rays (1253.6 eV) was used in these studies. Sputtering for the depth profiling experiments were carried out using a 5.5 keV Ar ions, with a sputter rate of $\sim 25 \text{ }\text{\AA}/\text{Min}$. XPS studies showed dramatically less corrosion products (oxidized aluminum the surface. Of particular note was the XPS study showing the absence or reduced concentration of copper in the top several hundred angstroms of the AA2024-T3 coupons coupon. Based



on these data we have postulated a model in which the sulfonated polyaniline, emeraldine base, or trimer coating plays a role in dissolving away the copper containing corrosion products. This would have a key role in eliminating the presence of the corrosion promoting galvanic couple between the aluminum and copper in AA2024-T3, thereby dramatically reducing the corrosion rate.

The results of the potentiodynamic studies are depicted in Figure 2, demonstrating the reduction in corrosion current obtained by the coatings. Potentiodynamic studies of emeraldine base and NSPAN/PVA coated AA2024-T3 both show a large decrease of the corrosion current ($\sim 10^{-8}$ A/cm²) as compared to the uncoated aluminum coupons ($\sim 10^{-7}$ A/cm²). In addition, the pitting potential is not observed for either coated coupon.

Potentiodynamic polarization curves of coated and uncoated AA2024-T3 are shown in

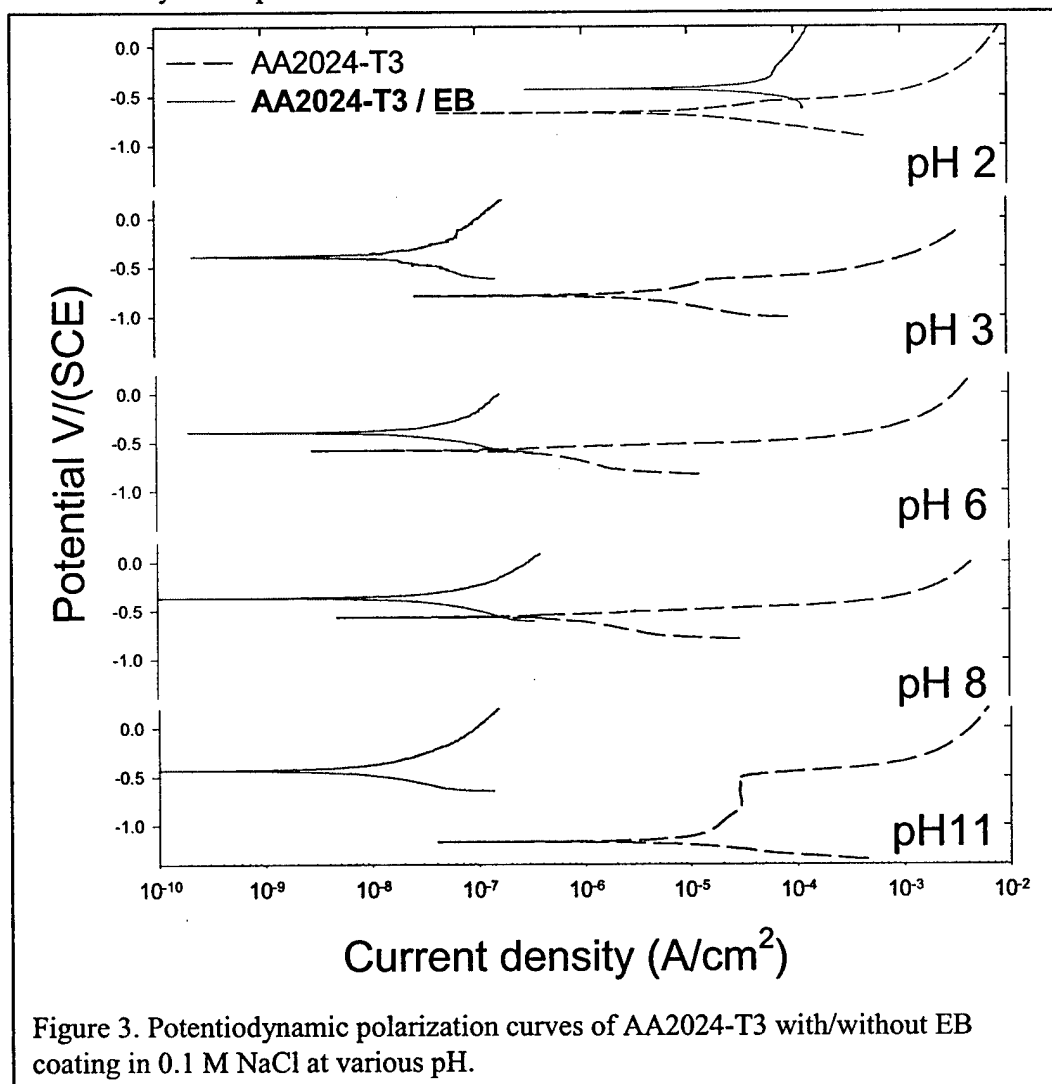


Fig. 3 for pH 2.0, 3.0, 5.7, 8.0, and 11.0 respectively. The corrosion rate for bare samples are high in acidic and alkaline solutions but low in neutral. This difference can be attributed to the change in the stability of the oxide film. Aluminum corrodes in aqueous solution because its oxides are soluble in many acids and bases. In highly acidic and alkaline solutions, the oxide film is highly soluble yielding Al^{3+} ions in the former and AlO_2^- (aluminate) ions in the latter. This leads to higher corrosion rate of the alloy. Whereas at neutral pH, the precipitate of aluminum hydroxide likely reduces the corrosion rate by protecting the alloy surface. Even though oxide film is stable in near neutral pH, pitting corrosion occurred because the aggressive ion chloride creates extensive localized attack by absorption at weak parts of the oxide film and

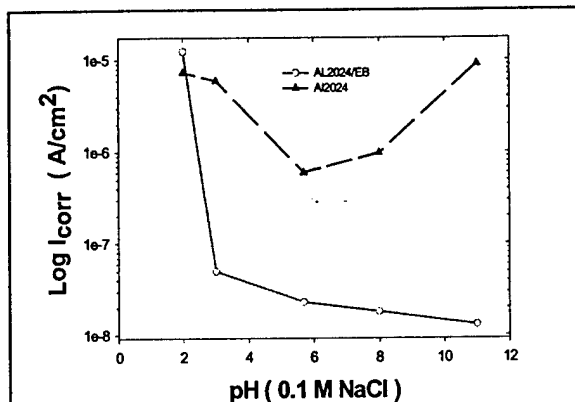


Figure 4. Dependence of corrosion current density of AA2024-T3 with/without EB coating on pH in 0.1 M NaCl solution.

lost in pH 3.0 and ceased at pH 2.0. Meanwhile, a color change from coppery to dark blue occurred for the polyaniline coatings at pH 3.0 and 2.0. We suggested that at this low pH the emeraldine base was doped to emeraldine salt and that the galvanic couple between the electrically conductive emeraldine salt and AA2024-T3 polarized positively the alloy and increased its corrosion current density.

| Depth (Å) | Corroded: 0.1 M NaCl, 66h, RT | | | | Pristine AA2024 | |
|-----------|-------------------------------|-------|--------|-------|-----------------|-------|
| | NSPAN/PVA/AA2024 | | AA2024 | | Cu/Al | Cl/Al |
| 0 | 0.0018 | 0.086 | 0.093 | 0.16 | ~0 | - |
| 25 | 0.014 | 0.035 | 0.072 | 0.088 | 0.0010 | - |
| 50 | 0.0098 | 0.042 | 0.060 | 0.067 | 0.013 | - |
| 100 | 0.013 | 0.019 | 0.049 | 0.068 | 0.016 | - |
| 150 | 0.014 | 0 | 0.043 | 0.067 | 0.019 | - |

little or no corrosion has occurred. In contrast, the non-coated coupons show a broadening of the high binding energy feature of the Al 2p core level and no metallic Al is visible, suggesting that the surface region has been corroded. The EB-coated coupons had stronger high binding energy features in the Al 2p core level as compared to the pristine and NSPAN/PVA coated coupons, but the thickness of the corroded surface region was less than that for non-coated Al2024-T3 as was evident upon sputtering. In Table 1 the ratios of Cu to Al and Cl to Al at various depths are presented for the most effective coating, NSPAN/PVA, non-coated AA2024-T3 and pristine AA2024-T3. The similarities between pristine AA2024-T3 and NSPAN/PVA coated AA2024-T3 are yet again striking. The copper content is negligible at the surface of those samples, increasing to ~1-2 Cu atoms per 100 Al at depths of 50-150 Å. In contrast, the corroded, non-coated AA2024-T3 coupons show an enrichment of Cu at the surface, ~9 Cu atoms per 100 Al, and the Cu to Al ratio is significantly higher through out the near surface region as compared to the pristine/non-coated and NSPAN/PVA/AA2024-T3 coated coupons. This is a very significant result, since enrichment of copper at the surface of aluminum alloys is considered to be one of the main factors in degrading the corrosion resistant oxide layer by causing localized accelerated

the formation of soluble complexes. For the polyaniline coated samples, the corrosion current density was decreased with the increase of solution pH. Polyaniline shifted the E_{corr} of AA2024-T3 in the positive direction for all pH. No pitting was found for coated samples in all these pH regions. Figure 4 gives the plots of corrosion current density against pH in 0.1M sodium chloride solution. At all pH, the coated samples exhibited lower corrosion rate than that of bare samples, with an exception at pH 2.0. The influence was found to be the most significant at pH = 11.0, where the coated samples exhibited approximately a 1000-fold decreased in corrosion current density compared to the bare samples. The corrosion resistance began to be

XPS depth profilings were carried out on coated and non-coated Al2024-T3 coupons exposed to an 0.1M NaCl bath as well as on pristine coupons. Even after 66h of exposure to the salt environment, the NSPAN/PVA coated coupons retain the same general core level features as the pristine alloy, indicating that

corrosion due to the formation of galvanic cells between the (noble) Cu atoms and the aluminum at the surface. Also worth noting is that the Cl to Al ratios are significantly lower in the near surface region for the NSPAN/PVA coated Al2024-T3 coupons as compared to the non-coated ones. Since chlorine is known to degrade the passive oxide layer on aluminum, reducing the amount of chlorine at the surface of the aluminum alloy also is likely to improve the corrosion resistance. The same trends in Cu/Al and Cl/Al ratios hold for EB coated Al2024-T3 coupons, Figure 5, though they are not as impressive as for the NSPAN/PVA system.

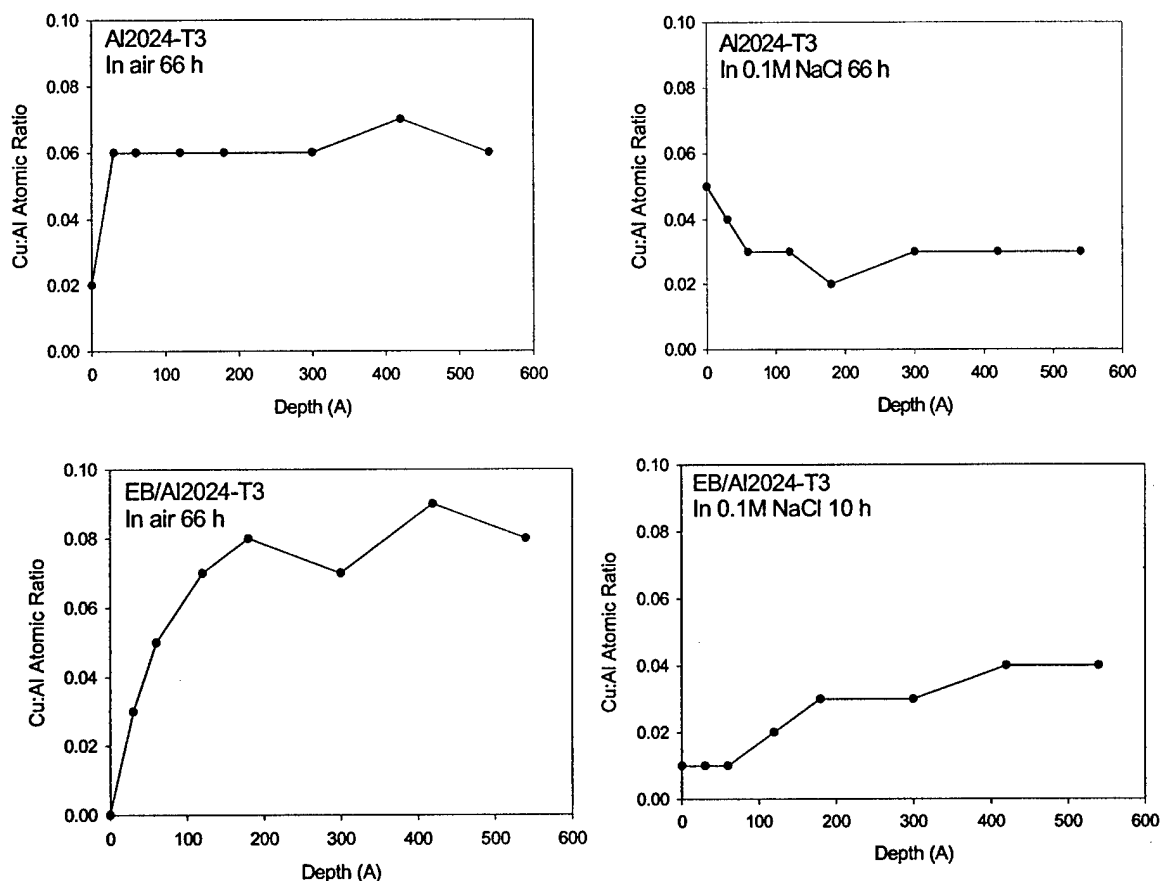
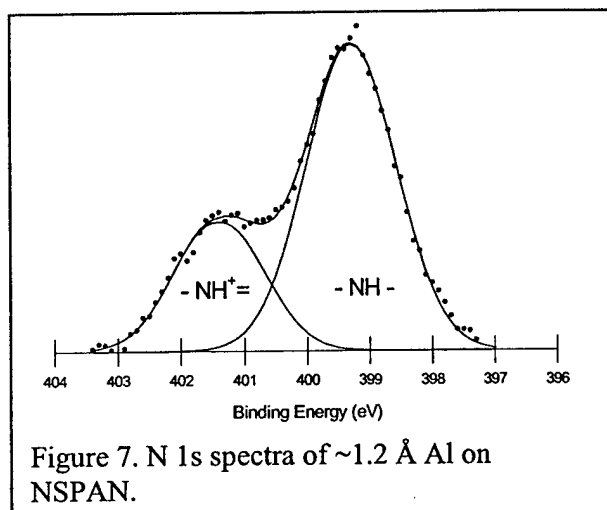
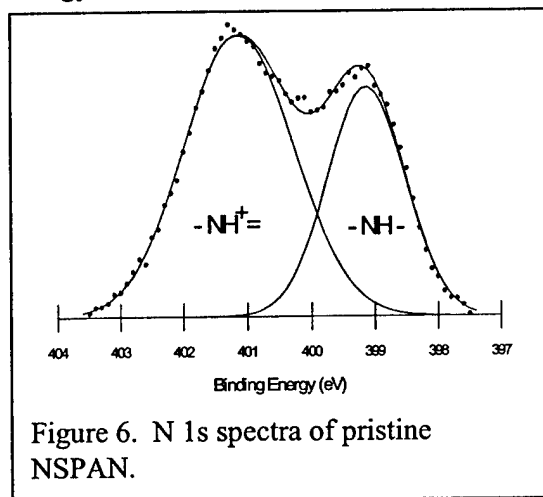


Figure 5. Cu:Al atomic ratios from XPS depth profiling (argon ion milling) of AA2024-T3. Top row: uncoated AA2024-T3; Bottom row: emeraldine base coated AA2024-T3; Left hand side: samples in air for 66 hour before XPS measurement; Right hand side: samples immersed in 0.1M NaCl for 66 hours before measurements.

To gain insight into the mechanism for corrosion protection we studied the XPS (ESCA) spectra of NSPAN films and NSPAN films with a monolayer of aluminum deposited while in ultrahigh vacuum. Two N 1s XPS peaks are observed centered at 401.12 eV and 399.13 eV and separated from each other by ~2 eV, Figures 6 and 7. Consistent with the literature we assign the lower binding energy N 1s peaks to amine nitrogen. The higher binding energy N 1s peak represents a more positively charged environment, and we assign those peaks to protonated

imine nitrogen. For the pristine NSPAN the higher binding energy N 1s imine peak contains about 64% of the total intensity, with the lower binding energy amine peak containing about 36% of the total intensity. The N 1s ESCA data after ~ 1.2 Å of aluminum has been evaporated onto the NSPAN (Figure 7) also are fit to two peaks, centered at 401.35 eV and 399.29 eV and again separated from each other by ~ 2 eV. The higher binding energy peak now contains about 28% of the total intensity, and the lower binding energy peak contains about 72% of the total intensity.

The S 2p ESCA data for pristine NSPAN can be fit to two peaks, each with a high binding energy shoulder due to spin-orbit splitting, centered at 167.20 eV and 168.35 eV. The higher



binding energy doublet contains about 26% of the total intensity, with the lower binding energy doublet containing about 74% of the total intensity. The S 2p ESCA data after ~ 1.2 Å of aluminum has been evaporated onto the NSPAN can be fit to three peaks, each with their high binding energy shoulder, centered at 167.41 eV, 168.32 eV and 169.28 eV. The highest binding energy doublet contains about 31% of the total intensity, the middle doublet contains about 35% of the total intensity, and the lowest binding energy doublet contains about 33% of the total intensity.

This ESCA determination of the oxidation state of NSPAN differs from that earlier reported for 50% and 75% sulfonated polyaniline, both of which were shown to be in the emeraldine oxidation state ($\sim 50\%$ oxidized). The higher oxidation state for the 100% sulfonated polyaniline and the bipolaron formation correlate with the lower density of states at the Fermi level and fewer localized spins for NSPAN as compared to 50% and 75% sulfonated polyanilines. The similar reduction in corrosion current for emeraldine base and NSPAN coated Al2024-T3 correlates with both polymers having a high density of imine-like sites. These imine sites may facilitate the extraction of copper from the surface of the Al2024-T3, thereby reducing the rate of corrosion through reduction or elimination of the Cu/Al galvanic cells formed at the surface of copper containing aluminum alloys (such as AA2024-T3) in salt solutions.

The immersion experiments

There are three main modes of corrosion protection that coatings could provide: (i) barrier protection (ii) cathodic/sacrificial protection and (iii) inhibitive/passivation protection.

Barrier protection is provided to the metal substrate by an intact coating which reduces the transport of ion or charge; the latter two modes may be termed active protection which can provide protection to damaged/non-covered areas.

To remove the barrier effect of coating and investigate the 'active' protection of polyaniline, polished but uncoated AA2024-T3 and cold rolled steel (CRS) alloy coupons were placed in a 0.1 M NaCl solution containing 0.2 % NSPAN. The pH of the solution was adjusted to 2.7 and 11.0 respectively, with an objective to studying the anticorrosion behavior corresponding to doped form (yellow solution, pH = 2.7) and undoped form (blue solution pH = 11.0) of NSPAN. The solutions were exposed to air. The control samples were immersed in equivalent solutions without NSPAN.

After a 60-day immersion, the CRS and AA2024-T3 coupons exposed to pH 2.7 and pH 11.0 NaCl solutions without NSPAN (control samples) showed severe pitting and general corrosion, and extensive corrosion products were observed. The alloy coupons exposed to pH 2.7 NaCl solution with NSPAN shown a significant amount of corrosion products, too. In contrast, the CRS and AA2024-T3 coupons exposed to pH 11.0 NaCl containing NSPAN solution remained shiny and smooth, with no visually observable corrosion. It appears that the undoped form of SPAN (at pH 11.0) suppressed the breakdown of the oxide film on metal surfaces and rendered it impermeable to aggressive ions. Microscopic examination revealed small dark pits, similar to those observed on the fresh samples. Polishing scratches were still visible on the unprotected alloy surfaces (Fig. 8 and Fig. 9), indicating a lack of significant general corrosion.

The above results indicate that both coating and solution of polyaniline achieve significant corrosion resistance for CRS and AA2024-T3 in neutral and alkaline sodium chloride corrosion environments. The anticorrosion behavior does not originate merely from a coating barrier effect. An electron-transfer exchange between the base forms of polyaniline and CRS may be partially responsible for the ability of polyaniline to maintain the passivity of the CRS specimen. However, polyaniline would not be expected to provide an anodic passive protection for Al alloys in the same way it protect ferrous alloys, since the open-circuit redox potential of polyaniline is considerably more positive than the pitting potential of aluminum.

We suggested that for the solution environments the corrosion resistance is mainly due to forming a film-like metal-polyaniline complex on metal surface in neutral and alkaline environments. The results of XPS depth profiling for EB coatings on AA2024-T3 and CRS indicated that iron and aluminum diffuse into the polymer film all the way to the outer surface, implying metal-nitrogen bonds with the imine nitrogen atoms of emeraldine base. An aluminum or iron ion generated in the corrosion reactions may form a stable coordination complex with several imine nitrogen atoms of the undoped form of polyaniline and NSPAN. The complexes stabilize the passive oxide film by reducing its dissolution rate. It is most likely that the metal-polyaniline complexes formed on anodic sites repair or 'heal' the cracks and ruptures before the damage spreads and the metal becomes active.

On the other hand, copper has a pronounced tendency in alkaline environments to form a complex with nitrogen atom. The electron pairs on the amine/imine nitrogen atoms of emeraldine base may be regarded as occupying one 3d, one 4s, and two 4p orbitals in the copper ion and form a stable multi-coordinated complex. Our XPS studies have demonstrated a reduction of the copper concentration at the top several hundred Å of the coated AA2024-T3 coupons. As a result, a model is suggested that the emeraldine base complexes copper from the

surface of AA2024-T3 thereby reducing the influence of Al/Cu galvanic couple, and decreasing the corrosion rate.



Figure 8 (a). CRS before corrosion (1x 500).



Figure 8 (b). CRS 60-day exposed to pH 11.0, 0.1 M NaCl + 0.2% NSPAN solution (1x 500).

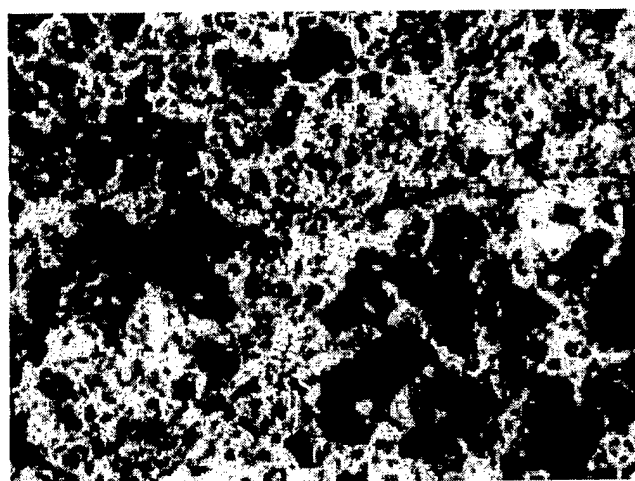


Figure 8(c). CRS 60-day exposed to pH 11.0, 0.1 M NaCl solution without NSPAN (1x 500).

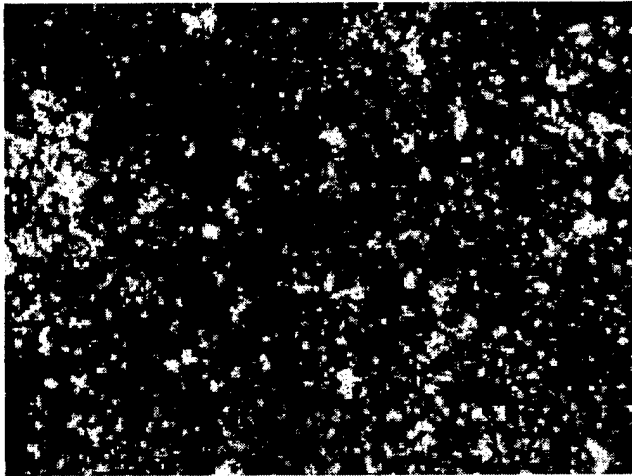


Figure 8 (d). CRS 60-day exposed to pH 2.7, 0.1 M NaCl + 0.2% NSPAN solution (1x 500).

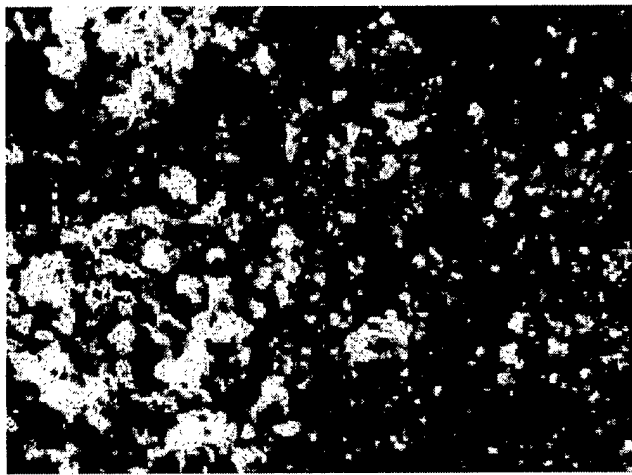


Figure 8(e). CRS 60-day exposed to pH 2.7, 0.1 M NaCl solution without NSPAN (1x 500).

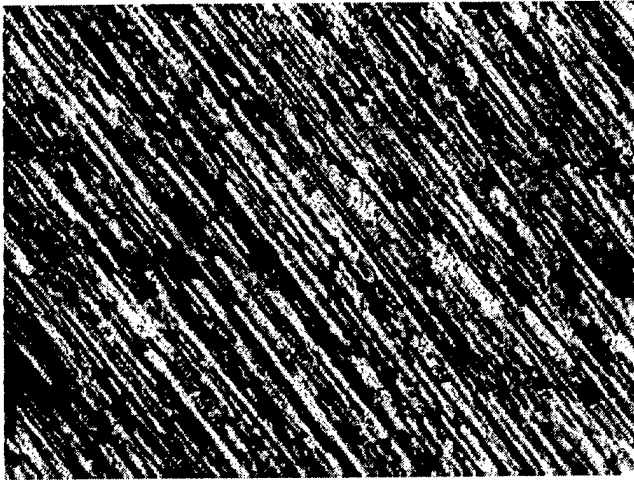


Figure 9 (a). AA2024-T3 before corrosion (1x 500).

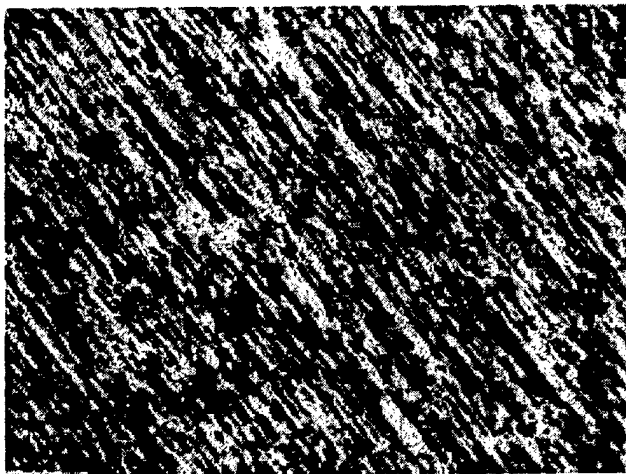


Figure 9 (b). AA2024-T3 60-day exposed to pH 11.0, 0.1 M NaCl + 0.2% NSPAN solution (1x 500).

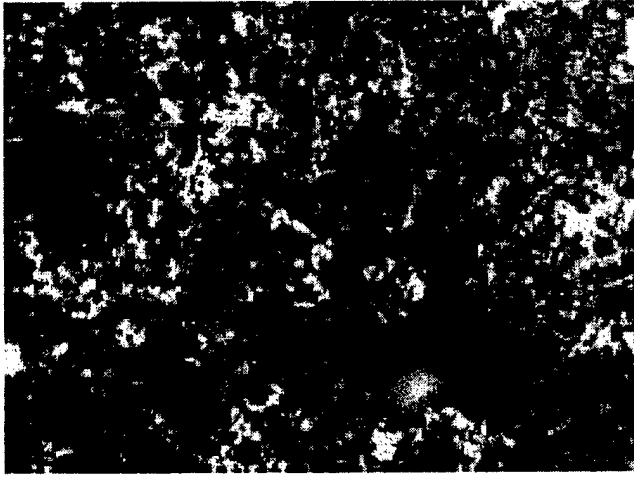


Figure 9 (c). AA2024-T3 60-day exposed to pH 11.0, 0.1 M NaCl solution without NSPAN (1x 500).

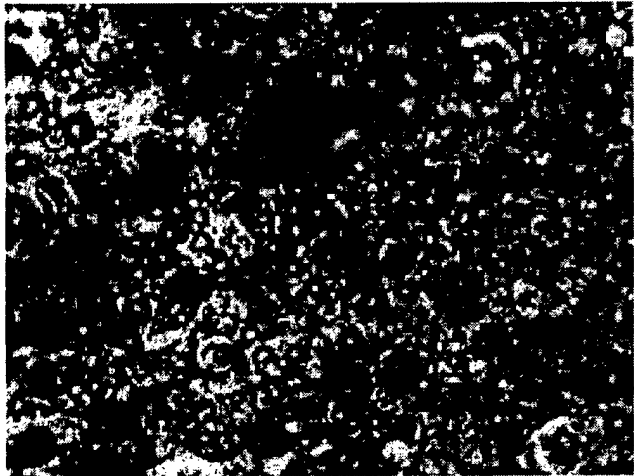


Figure 9 (d). AA2024-T3 60-day exposed to pH 2.7, 0.1 M NaCl + 0.2% NSPAN solution (1x 500).



Figure 9 (e). AA2024-T3 60-day exposed to pH 2.7, 0.1 M NaCl solution (1x 500).

2. Statistics:

- (1) Number of PI involved in the research project: 1
Arthur J. Epstein
- (2) Number of Post Docs supported under AFOSR: 1 full time equivalent
Mats Fahlman and Daike Wang
- (3) Number of graduate students supported by AFOSR: 1 full time equivalent
Julie Smallfield and Xiaolin Wei
- (4) Other researchers supported by AFOSR: 1 full time equivalent
Hong Guan and Pawan K. Kahol
- (5) Number of publications by PI that acknowledge this AFOSR support: 15

M. Fahlman, J.A.O. Smallfield, H. Guan, and A.J. Epstein, *X-ray Photoelectron Spectroscopy and Potentiodynamic Polarization Studies of Polymer Coated Al2024-T3*, to be published.

H. Guan and A.J. Epstein, *Effect of pH on the Anticorrosion Capability of Polyaniline Coatings and Solutions*, to be published.

M. Fahlman, H. Guan, S. Li, Y. Wei, and A.J. Epstein, *An X-ray Photoelectron Spectroscopy Study of the Metal-Organic Interface Between Iron and Aniline Trimers and Its Effect on Iron Oxide Growth in Humid and Salt Environments*, to be published.

A.J. Epstein, J.A.O. Smallfield, H. Guan, and M. Fahlman, *Fully Sulfonated Polyaniline (NSPAN) and Its Aluminum Interface: An ESCA Study*, **Polymer Preprints** **41** (2), 1737-1738 (2000).

M. Fahlman, X. Crispin, H. Guan, S. Li, J.A.O. Smallfield, Y. Wei, and A.J. Epstein, *Polyaniline-Metal Interfaces: Implications on Corrosion Protection of Steel and Aluminium Alloys*, **Polymer Preprints** **41** (2), 1753-1754 (2000).

G. Du, A. Burns, V.N. Prigodin, C.S. Wang, J. Joo and A.J. Epstein, *Anomalous Anderson Transition in Carbonized Ion-Implanted Polymer p-phenylenebenzobisoxazole*, **Physical Review B** **61**, 10142-10148 (2000).

A.J. Epstein, H. Guan, J.A.O. Smallfield, and M. Fahlman, *Corrosion Protection of Aluminum and Iron Alloys Using Polyanilines*, **Proceedings, Society of Plastics Engineers Annual Technical Conference (ANTEC 99, Volume 2)**, 2232-2234 (1999).

X.-L. Wei, Mats Fahlman, A.J. Epstein, *XPS Study of Highly Sulfonated Polyaniline*, **Macromolecules** **32**, 3114-3117 (1999).

G. Du, V.N. Prigodin, A. Burns, J. Joo, C.S. Wang, and A.J. Epstein, *Unusual Semimetallic Behavior of Carbonized Ion-Implanted Polymers*, **Physical Review B** **58**, 4485-4495 (1998).

A.J. Epstein, J.A.O. Smallfield, H. Guan, and M. Fahlman, *Corrosion Protection of Aluminum and Aluminum Alloys by Polyanilines: A Potentiodynamic and Photoelectron Spectroscopy Study*, **Synthetic Metals** **102**, 1374-1376 (1999).

M. Fahlman, D.D. Gebler, N.V. Piskun, D.-K. Fu, T.M. Swager, and A.J. Epstein, *Experimental and Theoretical Study of Ring-Substituent Induced Effects on the Structural and Optical Properties of Poly (p-pyridylvinylene-phenylenevinylene)s*, **Journal of Chemical Physics** **109**, 2031-2037 (1998).

M. Fahlman, H. Guan, J.A.O. Smallfield, and A.J. Epstein, *The Iron/Polyaniline Interface and Its Effect on Corrosion Protection of Iron and Cold Rolled Steel in Aqueous and Salt Environments*, **Proceedings, Society of Plastics Engineers Annual Technical Conference (ANTEC 98, Volume 2)**, 1238-1242 (1998).

M. Fahlman, S. Jasty, and A.J. Epstein, *Corrosion Protection of Iron/Steel by Emeraldine Base Polyaniline: An X-ray Photoelectron Spectroscopy Study*, **Synthetic Metals** **85**, 1323-1326 (1997).

M. Fahlman, J.A.O. Smallfield, and A.J. Epstein, *Corrosion Protection of Iron/Steel by Polyanilines: A Photoelectron Spectroscopy Study*, **Proc. Soc. of Plastics Engineers Annual Technical Conference (ANTEC 1997)**, Toronto, Ontario, April 27-May 2, 1997, 1330-1333 (1997).

M. Fahlman, D.D. Gebler, N.V. Piskun, D.-K. Fu, T.M. Swager, and A.J. Epstein, *Experimental and Theoretical Study of Ring-Substituent Induced Effects on the Structural and Optical Properties of Poly (p-pyridylvinylene-phenylenevinylene)s*, **Journal of Chemical Physics** **109**, 2031-2037 (1998).

(6) Number of invited presentations that acknowledged this AFOSR support: 12

M. Fahlman, S. Jasty, and A.J. Epstein, *Corrosion Protection of Iron/Steel by Emeraldine Base Polyaniline: an X-ray Photoelectron Spectroscopy Study*, **International Conference on Science and Technology of Synthetic Metals**, Snowbird, Utah, 28 July-2 August 1996.

M. Fahlman, J.A.O. Smallfield, and A.J. Epstein, *Corrosion Protection of Iron/Steel by Polyanilines: A Photoelectron Spectroscopy Study*, **Society of Plastics Engineers Annual Technical Conference (ANTEC 1997)**, Toronto, Canada, 27 April - 2 May 1997 [Society of Plastic Engineers 55th Annual Technical Paper, ANTEC '97, Volume 2, 1330-1333].

A.J. Epstein, *Corrosion Protection of Aluminum and its Alloys Using Electroactive Polymers*, Wright Patterson Air Force Base, May 20, 1997.

M. Fahlman, H. Guan, A.J. Epstein, and Y. Wei, *Polymer/Metal Interfaces and Their Effect on Corrosion Prevention*, **Meeting of the American Physical Society**, Los Angeles, California, 16-20 March 1998 [Bulletin of the American Physical Society 43, 439 (1998)].

A.J. Epstein, M. Fahlman, H. Guan, J.A.O. Smallfield, *The Iron/Polyaniline Interface and Its Effect on Corrosion Protection of Iron and Cold Rolled Steel in Aqueous and Salt Environments*, **Society of Plastics Engineers Annual Technical Conference (ANTEC 1998)**, Atlanta, Georgia, April 26-30, 1998.

A.J. Epstein, M. Fahlman, and H. Guan, *XPS and Potentiodynamic Study of Polyaniline Corrosion Protection of Aluminum and Its Alloys*, **International Conference on Science and Technology of Synthetic Metals**, Montpellier, France, 12-18 July 1998.

A.J. Epstein, *Polyanilines and their Effectiveness in Corrosion Protection of Iron and Aluminum Alloys*, **SEAM IV Workshop**, Polytechnic University, Brooklyn, NY, 5 December 1998.

A.J. Epstein, *Corrosion Protection of Iron and Aluminum Alloys by Polyaniline*, **Electroactive Polymers for Corrosion Protection Workshop**, Washington, DC, 5-6 January 1999.

A.J. Epstein, H. Guan, J.A.O. Smallfield, M. Fahlman, *Corrosion Protection of Aluminum and Iron Alloys Using Polyanilines*, **Society of Plastics Engineers Annual Technical Conference (ANTEC 1999)**, New York City, NY, 2-6 May 1999.

J.A.O. Smallfield, M. Fahlman, and A.J. Epstein, *Fully Sulfonated Polyaniline (NSPAN) and Aluminum Interface: an XPS Study*, **Meeting of the American Physical Society**, Minneapolis, Minnesota, 20-24 March 2000 [Bulletin of the American Physical Society 45, 512 (2000)].

M. Fahlman, X. Crispin, H. Guan, S. Li, J.A.O. Smallfield, Y. Wei, and A.J. Epstein, *Polyaniline-Metal Interfaces: Implications on Corrosion Protection of Steel and Aluminium Alloys*, **220th ACS National Meeting**, Washington, DC, August 20-24, 2000

A.J. Epstein, J.A.O. Smallfield, H. Guan, and M. Fahlman, *Fully Sulfonated Polyaniline (NSPAN) and Its Aluminum Interface: An ESCA Study*, **220th ACS National Meeting**, Washington, DC, August 20-24, 2000.

(7) Number of contributed presentations that acknowledged this AFOSR support: 8

W.P. Lee, K.R. Brenneman, A.J. Epstein, S. Shimizu, T. Saitoh, and M. Uzawa, *Audio Frequency AC Conduction in Sulfonated Polyanilines*, **Meeting of the American Physical Society**, Kansas City, Missouri, 17-21 March 1997 [Bulletin of the American Physical Society 42, 39-40 (1997)].

M. Fahlman, J.A.O. Smallfield, and A.J. Epstein, *Emeraldine Base Reduction/Oxidation (EMBRO) Corrosion Protection of Iron/Steel*, **Meeting of the American Physical Society**, Kansas City, Missouri, 17-21 March 1997 [Bulletin of the American Physical Society 42, 210 (1997)].

M. Fahlman, J.A.O. Smallfield, and A.J. Epstein, *X-ray Photoelectron Spectroscopy Study of Effectiveness of Using Emeraldine Base Polyaniline as Corrosion Protecting Coats on Aluminum*, **Meeting of the American Physical Society**, Kansas City, Missouri, 17-21 March 1997 [Bulletin of the American Physical Society 42, 212 (1997)].

P.K. Kahol, A. Raghunathan, B.J. McCormick, and A.J. Epstein, *A Magnetic Study of Sulfonated Polyanilines*, **Meeting of the American Physical Society**, Los Angeles, California, 16-20 March 1998 [Bulletin of the American Physical Society 43, 477 (1998)].

P.K. Kahol, A. Raghunathan, B.J. McCormick, and A.J. Epstein, *High Temperature Magnetic Susceptibility Studies of Sulfonated Polyanilines*, **International Conference on Science and Technology of Synthetic Metals**, Montpellier, France, 12-18 July 1998.

J.A.O. Smallfield, H. Guan, M. Fahlman, and A.J. Epstein, *Interface Between Polyaniline and Aluminum*, **Meeting of the American Physical Society**, Atlanta, Georgia, 20-26 March 1999 [Bulletin of the American Physical Society 44, 418 (1999)].

H. Guan and A.J. Epstein, *pH Effect on the Anti-Corrosion Capabilities of Polyaniline*, **31st ACS Central Regional Meeting**, Columbus, Ohio, 21-23 June 1999.

J.A.O. Smallfield, M. Fahlman, and A.J. Epstein, *Fully Sulfonated Polyaniline (NSPAN) and Aluminum Interface: an XPS Study*, **Meeting of the American Physical Society**, Minneapolis, Minnesota, 20-24 March 2000 [Bulletin of the American Physical Society 45, 512 (2000)].

(8) Awards and Honors received by the PI (life-time received):

SELECTED PROFESSIONAL ACTIVITIES OF PI:

| | |
|---------------|---|
| 1977,81,96 | Co-Organizer, International Conferences on Science and Technology of Synthetic Metals (ICSMs 1977, 1981) |
| 1977,81,96 | Co-Editor, Proc. ICSM 1977, ICSM 1981, and ICSM96 |
| 1979 | Visiting Professor, University of California, Los Angeles |
| 1980-90 | Adjunct Professor, Department of Physics, University of Florida, |
| 1977,81,88 | Member, Exec Committee, ICSMs; Program Comm., 1982, 84, 86, 90, 92 |
| 1984, 1992 | Visiting Professor, Université de Paris Sud, France |
| 1984, 1989 | Visiting Professor, Technion, Haifa, Israel |
| 1983 -1999 | Regional Editor, <i>Synthetic Metals</i> |
| 1985 -Present | Consultant, Xerox Corporation, DuPont, NCR, Hexcel |
| 1993 | Co-Organizer, Topical Conf. on Metallic Phase of Conducting Polymers; Co-editor of Proc. (Synth. Met. 65 (1994)) |
| 1994 | Co-Organizer, Fourth International Conference on Molecule-Based Magnets, Salt Lake City, Utah, 11-20 October 1994. |
| 1996 | Co-Organizer and Program Chair, International Conference on Science and Technology of Synthetic Metals, Snowbird, Utah, July 1996 |
| 1996 | Member, International Advisory Committee, International |

Conference on Molecule-Based Magnets, Osaka, Japan, July 1996
 1997 -Present Adjunct Professor of Chemistry, University of Utah, July 1997.
 1998 Member, International Advisory Committee, ICSMs 83, 84, 86, 90, 92, 98, 00
 1998 Member, International Advisory Committee, The VI th International
 Conference on Molecule-Based Magnets, Seignosse, France, 12-17
 September 1998
 1999 -Present Editor-in-Chief, *Synthetic Metals*
 2000-Present Member, EPIC (Edison Polymer Innovation Corporation) Board of
 Trustees
 2000-Present Regional Editor, Current Applied Physics

AWARDS AND DISTINCTIONS OF PI:

Fellow, American Physical Society, 1981.
Electronic Organic Materials, or, Is There Life After Silicon, **Frontiers of Science**
Lecture, University of Florida, Gainesville, Florida, 10 October 1984.
Frontiers in Polymers: Polaron Defects in Polyaniline, **Visiting Scholars/Sigma Xi**
Lecture, Departments of Physics and Chemistry, University of Rhode Island, Kingston,
 Rhode Island, 11 December 1987.
 "Hottest" Paper in Chemistry, Institute of Scientific Information, Jan.-Feb., 1990
 Distinguished Scholar Award, The Ohio State University, 1991.
 Finalist, Outstanding Teaching Award, The Ohio State University, 1994
Polymers-A New Frontier, **Frontiers of Science Lecture, University of Florida**,
 Gainesville, Florida, 2 October 1996.
 Distinguished University Professor, The Ohio State University, 1997
Light-Emitting Polymers and Their Devices, **Eastman Kodak Company**, Weissberger
 Williams Lecture Series, Rochester, NY, 9 December 1997.
 Technology Partnerships Alliance Award (OSU), 2000

3. *Transitions.*

a. PI/Institution: A.J. Epstein, The Ohio State University

b. Items of Transition:

U.S. Patent filed March 11, 1998 entitled "*Corrosion Protection of Aluminum and Aluminum Alloys Using Emeraldine Base Polyaniline.*"

c. Transition to: Under discussion